

In-situ inverse co-precipitation synthesis of CuCrO_2 /MWCNTs nanoparticles for thermal decomposition of ammonium perchlorate

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In this study, copper chromium oxide (CuCrO_2) nanoparticles as nanocatalyst were synthesized by inverse co-precipitation method and loaded on multiwall carbon nanotubes (MWCNTs) followed by investigating its catalytic effect on the thermal decomposition behavior of ammonium perchlorate (AP) using Differential Scanning Calorimetry (DSC). In this method, cupric nitrate trihydrate, ($\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$) and chromium nitrate nonahydrate, ($\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$) with a mole ratio of 1 : 1 were used. Characterization of CuCrO_2 /MWCNTs nanoparticles were performed by Thermo-Gravimetric-Differential Scanning Calorimetry (TG-DSC), Fourier Transform Infrared Spectroscopy (FT-IR), X-ray Diffraction Spectroscopy (XRD), and Field Emission Scanning Electron Microscopy (FE-SEM). The prepared catalysts were mixed with AP and the products were analyzed by DSC to determine the decomposition temperature of AP. The results showed that using 3 wt.-% nano- CuCrO_2 /MWCNTs catalyst lowered the decomposition temperature of AP by 87.34 °C. The total enthalpy, for this case, was 1367.40 J g⁻¹.

Key words: Ammonium perchlorate, Nanocatalyst, CuCrO_2 /MWCNTs nanoparticles, Thermal decomposition.

Introduction

Ammonium perchlorate is a white crystal chemical compound. It is stable in room temperature and has two orthorhombic and cubic crystal structures. This material is one of the most important parts in combustion of missile solid propellant [1, 2]. Ammonium perchlorate is the most common oxidizing agent in missile solid propellant and its unique property has pronouncing effects on the missile solid propellant [3]. Combustion properties of ammonium perchlorate have a pronouncing effect on burning rate of propellant [4]. Also, combustion properties are defined by an index named ammonium perchlorate combustion decomposition [5]. The lower the decomposition temperature of material, the better the combustion properties will be [6, 7]. One of the other indices is the enthalpy of combustion. The higher the indices, the better the combustion properties will be [8, 9]. In addition, thermal decomposition of ammonium perchlorate can be accelerated and performed in lower temperatures in presence of catalysts. These catalysts can go into the ammonium perchlorate structure or make a unique phase as a heterogeneous phase, and finally decreasing in decomposition temperature causes an increase in propellant rate and decrease in combustion delay time

[1]. Therefore, one way of improving these indices is to use one or more catalyst besides ammonium perchlorate. It is obvious that nano-catalysts are more proper than other typical catalysts [10, 11].

Today, many researches were reported in the field of the effects of different catalysts on thermal decomposition of ammonium perchlorate in solid propellant, especially nano particles, due to their very small particle size and low surface area. Researchers have come to conclusion that catalysts accelerate burning rate of propellant by accelerating ammonium perchlorate thermal decomposition [12-15].

Many reports show the use of catalysts or nano-catalysts in this topic. Xujie Yang *et al.* [16] lowered decomposition temperature of ammonium perchlorate by using MgO as catalyst. Lizhi Zhang *et al.* [17] have studied Fe_2O_3 as catalyst and showed a decrease in decomposition temperature of ammonium perchlorate from 436.4 °C to 387.5 °C.

In another study, Linsheng *et al.* [18] utilized CuFe_2O_4 for the same purpose and reported a decrease in temperature from 445 °C to 351 °C. Using Cu_2O as physical admixture by ammonium perchlorate showed a decrease in decomposition temperature from 439 °C to 348 °C [19]. Alizade-Gheshlaghi *et al.* [20] have used CuO, Co_3O_4 , and CuCo_2O_4 as catalysts, and reported a decrease in decomposition temperature from 441.61 °C to 353.14 °C, 351.54 °C, and 340.83 °C, respectively. In another study, physical admixture of CuCr_2O_4 with ammonium perchlorate caused a decrease in decomposition temperature of ammonium

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perchlorate from 467 °C to 349 °C [21]. They applied an electrochemical approach; a method which is totally different from what it was used in this study. FengSheng Li *et al.* [22] used Ni/CNTs catalyst and experienced temperature decrease of ammonium perchlorate decomposition from 446.5 °C to 346 °C. Feng Li *et al.* [23] used CNTs, CoAl-MMO, and CoAl-MMO/CNT as catalysts, and reported a decomposition temperature of ammonium perchlorate from 444 °C to 355 °C, 297 °C, and 271 °C, respectively. Cui Ping *et al.* [24] used Cu, compound of Cu and CNT, and Cu/CNT followed by physical mixing with ammonium perchlorate and reported a decrease in decomposition temperature of this material from 478.1 °C to 395.4 °C, 363.2 °C, and 351.8 °C, respectively. On the other hand, using carbon nano-tubes as catalysts are reported in various researches [25]. In most works, using pure carbon nano-tubes is an essential [25]. The used carbon nano-tubes as substrate for catalysts, improves catalytic activity because of their unique properties like small size and high surface area [26].

Although, there have been several studies in literature in this field, using modified carbon nano-tubes as catalyst in thermal decomposition of ammonium perchlorate, there is no report in approaching to CuCrO₂/MWCNTs. Therefore, in this study, this material is used as catalyst in thermal decomposition of ammonium perchlorate. By this study, the effects of temperature decrement and enthalpy increment in decomposition of ammonium perchlorate have been discussed.

Experimental Procedures

Reagents and Materials

The used reagents and analytical instruments include multi-wall carbon nanotubes (MWCNTs) with approximate diameter 20-30 nm (National Iranian Oil Company), cupric nitrate trihydrate (Cu (NO₃)₂ · 3H₂O), chromium nitrate (Cr (NO₃)₃ · 9H₂O, India Co LOBA Chemie), ammonium hydroxide (NH₄OH, Merck). All used chemicals in the experiments were of analytical purity.

Instrumentation

The crystal phase of the as-prepared products was identified by powder X-ray diffraction method XRD using Co-K α radiation (λ : 1.74056 Å) at a scan rate of 4 °C/min. The average crystallite size of the powders was measured by X-ray line-broadening technique employing the Scherrer's equation. The nanostructural morphology of the final products was characterized by a Hitachi S416002, Holland Field Emission Scanning Electron Microscopy (FE-SEM). Prior to analysis, a thin layer of Au was evaporated onto the specimens for desired electrical conductivity. The nature of metal oxides of the final product was characterized by a Fourier Transform Infrared Spectroscopy (FT-IR). The

FT-IR spectra were recorded on a Bruker TENSOR 27 FT-IR spectrometer in KBr pellets with a resolution of 4 cm⁻¹ using 32 scans for each sample. Thermal decomposition procedure of the as-obtained mixture of CuCrO₂/MWCNTs and AP was studied by TG-DSC (Metler Toledo, Switzerland).

Purification of MWCNTs

The raw MWCNTs need to be purified before preparing CuCrO₂/MWCNTs nanostructure. MWCNTs were calcined at 350 °C for 2 h to remove amorphous carbon. The calcined MWCNTs (1 g) were dispersed in 100 mL HNO₃ at the concentration of 7.0 mol/L and via ultrasonic processing for 15 min, then refluxing at 120 °C for 10 h with stirring. The products were rinsed with deionized water until the solution was neutral, and finally dried under the oven 60 °C.

Synthesis of CuCrO₂/MWCNTs Nanopartices via Inverse Co-Precipitation

The CuCrO₂/MWCNT_s catalysts were synthesized by inverse coprecipitation route. In a typical synthesis procedure, 0.005 mol Cu(NO₃)₂ · 3H₂O and 0.01 mol Cr(NO₃)₃ · 9H₂O were dissolved in 100 mL deionized water to obtain a mixed metal nitrate solution. Appropriate amount of Cu(NO₃)₂ · 3H₂O and Cr(NO₃)₃ · 9H₂O in stoichiometric ratio of Cu : Cr = 1 : 1 were dissolved in deionized water, After stirring for 60 min, Then 0.2 g nanotube, multi-walled carbon was added to the ammonia solution and for 30 min in ultrasonic dispersed, the solution metal nitrate was added to solution ammonia. The pH of the solution was adjusted to pH 9.0 by slowly dropping metal nitrate solution and continued stirring for 1.0 h. The fine precipitates of basic copper chromium oxide nanoparticles loaded on multiwall carbon nanotubes were filtered, washed with distilled water, and dried at 110 °C to a constant weight. Then, CuCrO₂/MWCNTs nanocatalyst produced by tube furnace under argon gas at a rate 150 cm³/min, was calcined at temperatures 600 °C in the argon for 2.0 h at a heating rate of 20 °C min⁻¹ to obtain the final black CuCrO₂/MWCNT_s nanocatalysts. Then, the CuCrO₂/MWCNTs nanocatalysts were mixed physically with 3 wt% AP and were as analyzed by TG-DSC.

Results and Discussion

Figure 1 shows the FT-IR spectra of the unmodified and modified MWCNTs. The FT-IR spectra of carboxylation carbon nanotubes (MWNTs-COOH) group peak can be seen at 1713 cm⁻¹, hydroxyl group peak at 3384 cm⁻¹, methylene (-CH₂-) symmetric or asymmetric group peak at 2921 cm⁻¹, and inner planes bending vibrations hydroxyl group peak at 1384 cm⁻¹. The only index peak, related to purification and functionalization of the MWCNTs FT-IR results, were observed around 1713 cm⁻¹ which can probably be

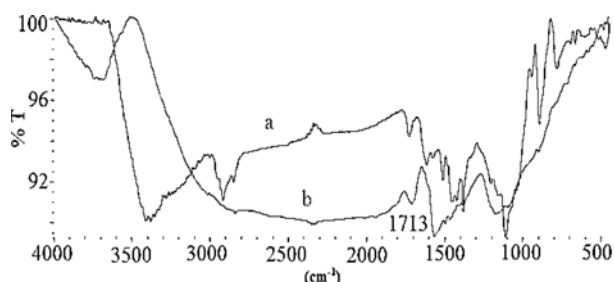


Fig. 1. FT-IR patterns of carbon nanotubes: (a) unmodified carbon nanotubes; (b) carbon nanotubes purified by acid.

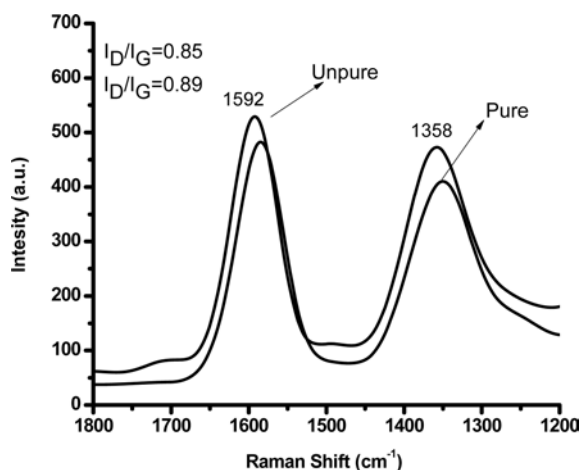


Fig. 2. Raman spectra of unpure-MWCNTs and acid-treated MWCNTs.

attributed to MWCNTs purification.

Figure 2 shows the Raman spectra of impure MWCNTs and acid-treated MWCNTs. The D band is attributed to defects in the disorder induced modes (or sp^3 -hybridized carbons) and G band related to graphitic wall inner planes vibrations (or sp^2 -hybridized carbons). The D band at 1358 cm^{-1} and G band at 1592 cm^{-1} characterized by Raman spectroscopy spectra, showed I_D/I_G area 0.85 and 0.89, respectively [27].

The crystalline structure of catalyst was characterized by XRD. As shown in Figure 3 the patterns can be readily referred to Copper Chromium Oxide (JCPDS n0. 01-074-0983) and graphite (JCPDS no. 00-001-0640). In the pattern assigned to Copper, diffraction peaks at around 36.59° , 41.11° , 42.24° , 47.83° , 51.53° , 56.18° , 60.61° , 65.88° , 73.93° , 76.85° , 77.79° , 84.46° , 85.43° , and 26.14° correspond to the (006), (101), (012), (104), (015), (009), (107), (018), (110), (113), (0012), (0111), (116), reflections, respectively. Diffraction peak at 30.71° can be indexed to (002) reflection of the MWCNTs. The large peak widths are ascribed to the formation of nanosized particles of $\text{CuCrO}_2/\text{MWCNT}_s$. The mean crystallite sizes were calculated by Scherrer equation $(0.9\lambda)/(\beta\cos\theta)$, by measuring the line broadening of main intensity peak, where λ is the wavelength of Co K α radiation, β is the full width at half-maximum, and θ is the Bragg's angle [28, 29] using the (012) peak

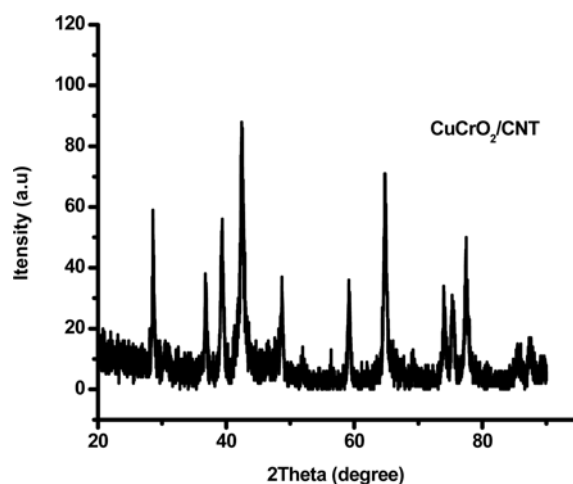


Fig. 3. XRD patterns of the $\text{CuCrO}_2/\text{MWCNT}_s$ samples via inverse co-precipitation reaction method.

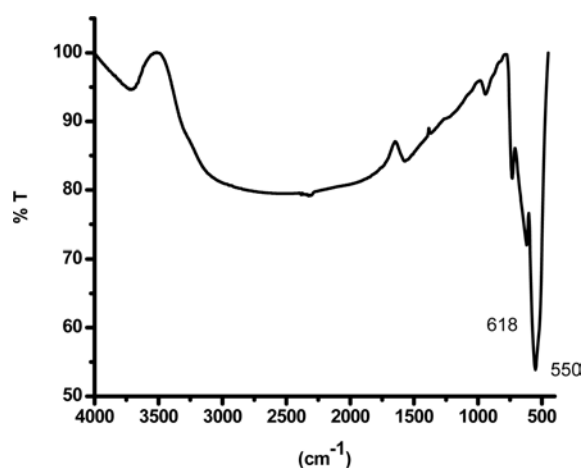


Fig. 4. FT-IR of the $\text{CuCrO}_2/\text{MWCNT}_s$ synthesized by inverse co-precipitation.

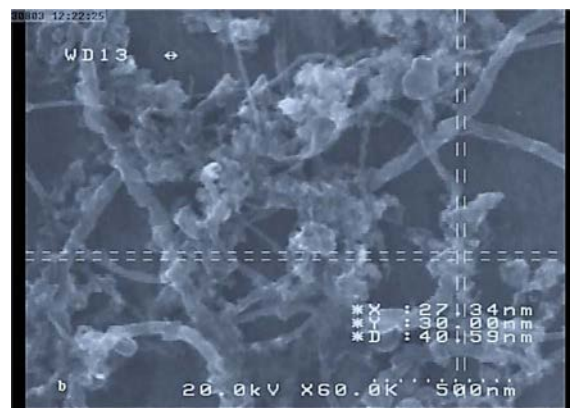


Fig. 5. FE-SEM image of $\text{CuCrO}_2/\text{MWCNT}_s$ nanocatalyst.

($2\theta = 42.24^\circ$) which is 11 nm.

The Fourier transform infrared (FT-IR) spectrum of $\text{CuCrO}_2/\text{MWCNT}_s$ is shown in Figure 4. Transition metal chromite spinel is expected to exhibit the characteristic absorption bands in the shortwave region around $618\text{--}550\text{ cm}^{-1}$ due to M-O and Cr-O stretching frequencies, respectively. The IR band for chromite

sample could be attributed to the stretching vibration of the Cr-O bands of chromium atoms in the tetragonal environment of the O atom.

Figure 5 shows a Field Emission Scanning Electron Microscopy (FE-SEM) of $\text{CuCrO}_2/\text{MWCNTs}$ surface morphology. The micrograph shows the formation of powder consisting of spherical structure particles with an average particle size of 40 nm.

Study on Thermal Decomposition of AP in the Presence of $\text{CuCrO}_2/\text{MWCNTs}$ Nanocatalyst

Figure 6 shows the DSC curve for pure AP and for physical mixture of AP and 3 wt.-% $\text{CuCrO}_2/\text{MWCNTs}$ at $10^\circ\text{C min}^{-1}$. The endothermic DSC peak at 247.44°C in pure AP (Figure 6a) is due to the crystallographic transition from orthorhombic to cubic form. This transition remains unaltered (or partially altered) after the addition of $\text{CuCrO}_2/\text{MWCNTs}$. In pure AP, the first low temperature exothermic peak (LTD) at 309.52°C is attributed to the partial decomposition of AP while the second and main high temperature exothermic (HTD) at

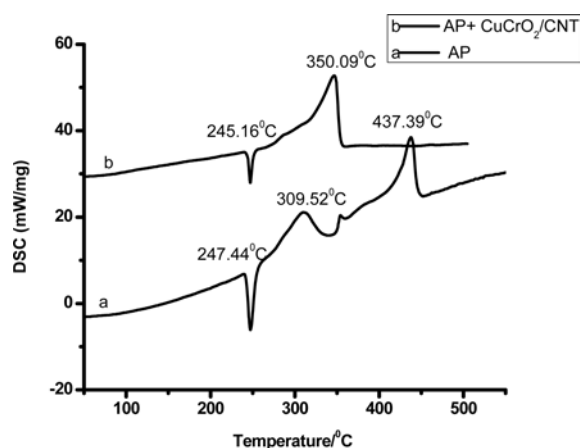


Fig. 6. DSC patterns for samples of (a) pure AP and (b) physical mixtures of AP and 3 wt. % $\text{CuCrO}_2/\text{MWCNTs}$ at $10^\circ\text{C min}^{-1}$.

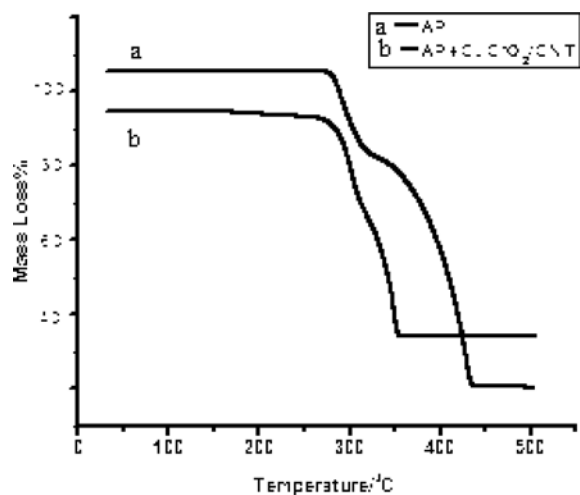


Fig. 7. TG patterns of different samples: (a) pure AP, (b) AP/3 wt.-% nanosized $\text{CuCrO}_2/\text{MWCNTs}$.

437.39°C corresponds to complete decomposition of intermediate products into volatile products.

After the addition of $\text{CuCrO}_2/\text{MWCNTs}$, remarkable changes were observed in high temperature decomposition (HTD) of AP. Figure 6b shows the decomposition of AP in the presence of $\text{CuCrO}_2/\text{MWCNTs}$ at heating rate, $10^\circ\text{C min}^{-1}$. The position of the exothermic strongly depends on the size of the functionalized MWCNTs. Compared to pure AP, the HTD has been observed to shift from 437.39°C (pure AP) to 353.9°C (AP and 3 wt.-% $\text{CuCrO}_2/\text{MWCNTs}$), at $10^\circ\text{C min}^{-1}$. This drastic decrease in temperature by 87.30°C indicates an efficient catalytic effect on the thermal decomposition of AP. The decrease is more significant in $\text{CuCrO}_2/\text{MWCNTs}$ due to the synergistic action of the binary (AP and 3 wt.-% $\text{CuCrO}_2/\text{MWCNTs}$) causing an enhancement in the catalytic activity. Such a marked reduction in HTD is also attributed to the presence of a large number of active sites, higher surface area, and smaller size of synthesized $\text{CuCrO}_2/\text{MWCNTs}$. Another interesting observation was a high heat release of 1367.40 J g^{-1} (3 wt.-% $\text{CuCrO}_2/\text{MWCNTs}$) compared to 410.58 J g^{-1} for pure AP, which is the highest value achieved so far by using $\text{CuCrO}_2/\text{MWCNTs}$ catalyst.

Figure 7 shows the TG curves at $10^\circ\text{C min}^{-1}$ for pure AP and mixtures of AP and 3 wt.-% $\text{CuCrO}_2/\text{MWCNTs}$. As it is observed, the thermal decomposition curve of pure AP shows a two-steps weight loss. At low temperature (331°C), in which weight loss is 15%, it can be related to partial decomposition of AP and formation of intermediate NH_3 and HClO_4 by dissociation and sublimation, respectively. At high temperature (437°C), in which weight loss is 85%, it can be related to complete decomposition of the intermediate volatile products. In the presence of $\text{CuCrO}_2/\text{MWCNTs}$ nanocatalyst, TG curve shows that the weight loss step is a one step process which means a complete decomposition of AP.

As the above results show, the $\text{CuCrO}_2/\text{MWCNTs}$ have presented very excellent catalytic properties. As the enthalpy values show, it confirmed that $\text{CuCrO}_2/\text{MWCNTs}$ played a catalytic role in this study. It is probably due to the fact that during thermal decomposition of AP, the temperature rises to above 350°C and at the same time the MWCNTs are burning too. This can be the reason for increasing the enthalpy of AP plus $\text{CuCrO}_2/\text{MWCNTs}$.

Conclusions

The following results were obtained.

1. The inverse co-precipitation method showed a successful route for $\text{CuCrO}_2/\text{MWCNTs}$ preparation.
2. The optimum temperature for calcination was 600°C .
3. The peaks at 1713 cm^{-1} and 3384 cm^{-1} in FT-IR showed a nature of carboxylation and hydroxyl group for carbon nanotubes.

4. The D band at 1358 cm^{-1} and G band at 1592 cm^{-1} characterized by Raman spectroscopy spectra, showed I_D/I_G area of 0.85 and 0.89, respectively.

5. The diffraction peaks of MWCNTs at 30.71° can be indexed to (002) and at 42.24° to (012) reflection plane for copper chromium oxide, respectively.

6. The average particle size was determined 40 nm.

7. The nature of metal oxides of final product characterized by FT-IR, showed a $\text{Cr}_2\text{O}_4^{2-}$ group.

8. The peak of the high temperature decomposition of AP was decreased about 87.34°C .

9. High released heat (ΔH) is 1367.40 J g^{-1} for mixed samples of AP and 3 wt. % $\text{CuCrO}_2/\text{MWCNTs}$, while it is 410.58 J g^{-1} for pure AP.

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